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(54) 【発明の名称】 オゾンインジケーター及びオゾン濃度測定方法

(57)【要約】

【課題】特に高濃度オゾン雰囲気下でもオゾン濃度等の 測定が可能なオゾンインジケーターを提供する。

【解決手段】少なくとも①オゾン検知用インキからなる変色層及び②当該変色層上の一部又は全部に形成されたオーバーコート層を有することを特徴とするオゾンインジケーター、及びそれを用いたオゾン濃度測定方法。

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【特許請求の範囲】

【請求項1】少なくとも①オゾン検知用インキからなる変色層及び②当該変色層上の一部又は全部に形成されたオーバーコート層を有することを特徴とするオゾンインジケーター。

【請求項2】オゾン検知用インキが、第一アミノ基及び 第二アミノ基の少なくとも1種のアミノ基を有するアン トラキノン系染料を含有する請求項1記載のオゾンイン ジケーター。

【請求項3】オゾン検知用インキが、さらに4級アンモ 10 ニウム塩型のカチオン系界面活性剤を含有する請求項2 記載のオゾンインジケーター。

【請求項4】4級アンモニウム塩型のカチオン系界面活性剤が、アルキルトリメチルアンモニウム塩である請求項3記載のオゾンインジケーター。

【請求項5】オゾン検知用インキが、増量剤を含有する 請求項2~4のいずれかに記載のオゾンインジケータ

【請求項6】オゾン検知用インキが、樹脂系バインダーを含有する請求項2~5のいずれかに記載のオゾンイン 20 ジケーター。

【請求項7】オーバーコート層が造膜性高分子を含む請求項1~6のいずれかに記載のオゾンインジケーター。 【請求項8】造膜性樹脂が水溶性高分子の少なくとも1種である請求項7記載のオゾンインジケーター。

【請求項9】オーバーコート層が着色剤を含有しない請求項1~8のいずれかに記載のオゾンインジケーター。 【請求項10】請求項1~9のいずれかに記載のオゾンインジケーターをオゾン雰囲気中に設置した後、変色層の変色による色差又は変色域によりCT値を求めることを特徴とするオゾン濃度の測定方法。

【請求項11】オゾン雰囲気中のオゾン濃度が1000 ppm以上である請求項10記載の測定方法。

【発明の詳細な説明】

[0001]

【発明の属する技術分野】本発明は、オゾンインジケーター及びオゾン濃度測定方法に関する。

[0002]

【従来技術】オゾンは、その殺菌性等に優れているため、食品、器具類等の殺菌・消毒、あるいは病院の手術 40室のような一定雰囲気中における殺菌・消毒又は消臭に利用されている。その一方で、オゾンは、毒性がきわめて強く、人体にも影響を及ぼすので、その許容濃度に限界がある。他方、光化学スモッグ予報においては、大気中のオキシダント濃度が重要な要素となる。

【0003】このため、オゾン濃度を監視すべく、その 検知方法が種々開発されている。従来におけるオゾン (オキシダント)検知方法としては、主として下式 (1)の反応による変色が利用されている。 $\begin{array}{c}
2\\
\text{(O)}\\
\text{KI} \rightarrow \text{I}_{2} & \cdots \text{(1)}
\end{array}$

この原理を利用した検知方法としては、例えばヨウ化カリ溶液にオゾンを含むガスを導入し、発生するヨウ素の量に比例した変色度合いを比色計により光学的に測定する方法、あるいは簡便なタイプの検知管による方法等が従来より知られている。

[0004]

【発明が解決しようとする課題】しかしながら、これらの検知方法はいずれも比較的低濃度のオゾンの検知を目的としたものであり、高濃度のオゾン検知には適していない。すなわち、これらの方法により高濃度のオゾンを検知しようとしても、瞬時に変色してしまうため、オゾンの有無は検知できたとしても、オゾン濃度、CT値(オゾン濃度と暴露時間の積算値)等を定量的に検知することはできない。

【0005】従って、本発明の主な目的は、特に高濃度 オゾン雰囲気下でもオゾン濃度等の測定が可能なオゾン インジケーターを提供することにある。

0 [0006]

【課題を解決するための手段】本発明者は、かかる従来 技術の問題に鑑みて鋭意研究を重ねた結果、特定の構成 をもつオゾンインジケーターにより上記目的を達成でき ることを見出し、本発明を完成するに至った。

【0007】すなわち、本発明は、少なくとも①オゾン 検知用インキからなる変色層及び②当該変色層上の一部 又は全部に形成されたオーバーコート層を有することを 特徴とするオゾンインジケーターに係るものである。

[0009]

【発明の実施の形態】本発明のオゾンインジケーターは、少なくとも①オゾン検知用インキからなる変色層及び②当該変色層上の一部又は全部に形成されたオーバーコート層を有することを特徴とする。

【0010】上記変色層は、オゾンの存在下で変色する層であり、主としてオゾン検知用インキにより形成される。本発明における「変色」とは、当初の色(明度、色相等)が変わるすべての現象を包含する概念であり、例えば褪色、消色、発色等を含む。変色層は基材上に形成しても良いし、変色層自体に成形性(形状保持性能)があれば基材なしでも形成できる。

【0011】基材を用いる場合、その基材の種類は特に制限されず、例えば金属・合金、木質材料、紙、セラミックス、ガラス、コンクリート、プラスチックス、繊維類(不織布、織布、その他の繊維シート)、これらの複合材料等を用いることができる。

50 【0012】変色層を形成するためのオゾン検知用イン

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キは、オゾン雰囲気 (オゾンを含有する雰囲気) に晒されることにより変色するものであれば特に制限されず、公知のインキ又は市販品を用いることができる。例えば、ヨウ化カリウム、トリフェニルメタン系ロイコ体、p-n-ブトキシアニリン等を用いたインキを用いることができる。

【0013】本発明では、オゾン検知用インキとして特に第一アミノ基及び第二アミノ基の少なくとも1種のアミノ基を有するアントラキノン系染料を含有するインキを用いることが望ましい。

【0014】本発明で用いるアントラキノン系染料は、アントラキノンを基本骨格とし、第一アミノ基及び第二アミノ基の少なくとも1種のアミノ基を有する限りは特に制限されず、公知のアントラキノン系分散染料等も使用できる。上記アミノ基は、2以上有していても良く、これらは互いに同種又は相異なっても良い。

【0015】このようなアントラキノン系染料として は、例えば1, 4 - ジアミノアントラキノン (C.I.Disperse Violet 1) $1-r \le J-4-t \le J-2-$ メトキシアントラキノン (C.I.Disperse Red 4)、1-アミノー4ーメチルアミノアントラキノン(C.I.Disper se Violet 4) $\langle 1, 4-iir \rangle = 2-iir \rangle$ トラキノン (C.I.Disperse Red 11)、1-アミノー2 ーメチルアントラキノン (C.I.Disperse Orange 11)、 1-アミノー4-ヒドロキシアントラキノン(C.I.Disp erse Red 15) (1, 4, 5, 8-7)ラキノン(C.I.Disperse Blue 1)、1,4ージアミノ -5-ニトロアントラキノン (C.I.DisperseViolet 8) 等を挙げることができる (カッコ内は染料番号)。その 他にも C.I.Solvent Blue 14、C.I.Solvent Blue 63、 C.I.Solvent Violet 13, C.I.SolventViolet 14, C.I.S olvent Red 52, C.I.Solvent Red 114, C.I.Vat Blue 2 1, C.I.Vat Blue 30, C.I.Vat Violet 15, C.I.Vat Vio 1et 17, C.I.Vat Red 19, C.I.Vat Red 28, C.I.Acid B lue 23, C.I. Acid Blue 80, C.I. Acid Violet 43, C.I. Acid Violet 48, C.I. Acid Red 81, C.I. Acid Red 83, C.I.Reactive Blue 4, C.I.Reactive Blue 19, C.I.Dis perse Blue 7 等として知られている染料も使用するこ とができる。これらのアントラキノン系染料は、単独で 又は2種以上併用することができる。これらアントラキ ノン系染料の中でも、C.I Disperse Blue7、C.I Disper se Violet 1 等が好ましい。また、本発明では、これら のアントラキノン系染料の種類(分子構造等)を変える ことによって、オゾンの検知感度の制御を行うこともで

【0016】本発明では、上記アントラキノン系染料を含有するインキ中に4級アンモニウム塩型のカチオン系界面活性剤をさらに含有することがより好ましい。

【0017】上記4級アンモニウム塩型のカチオン系界 面活性剤(以下単に「カチオン系界面活性剤」ともい う)としては、特に制限されず、通常はアルキルアンモニウム塩を用いることができ、これは市販品も使用できる。また、これらは1種又は2種以上で使用することが

る。また、これらは1種人は2種以上で使用することができる。本発明では、これらカチオン系界面活性剤を前記アントラキノン系染料と併用することによって、より優れたオゾン検知感度を得ることができる。

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【0018】これらカチオン系界面活性剤の中でも、アルキルトリメチルアンモニウム塩、ジアルキルジメチルアンモニウム塩等が好ましい。具体的には、塩化ヤシア10 ルキルトリメチルアンモニウム、塩化ベヘニルトリメチルアンモニウム、塩化ベーニルトリメチルアンモニウム、塩化ベーニルトリメチルアンモニウム、塩化ウウリルトリメチルアンモニウム、塩化ジオクチルジメチルアンモニウム、塩化ジステアリルジメチルアンモニウム、塩化アルキルベンジルジメチルアンモニウム等が挙げられ、特に塩化ラウリルトリメチルアンモニウムが好ましい。【0019】本発明のインキでは、必要に応じて樹脂系

【0019】本発明のインキでは、必要に応じて樹脂系 バインダー、増量剤、溶剤等の公知のインキに用いられ 20 ている成分を適宜配合することができる。

【0020】樹脂系バインダーとしては、基材の種類等に応じて適宜選択すれば良く、例えば筆記用、印刷用等のインキ組成物に用いられている公知の樹脂成分をそのまま採用できる。具体的には、例えばマレイン酸樹脂、アミド樹脂、ケトン樹脂、アルキルフェノール樹脂、ロジン変性樹脂、ポリビニルブチラール、ポリビニルピロリドン、セルロース系樹脂、アクリル系樹脂、酢酸ビニル系樹脂等を挙げることができる。

【0021】増量剤としては、特に制限されず、例えば ベントナイト、活性白土、酸化アルミニウム、シリカゲ ル等を挙げることができる。その他にも公知の体質顔料 として知られている材料を用いることができる。この中でも、多孔質のものが好ましく、特にシリカゲルがより 好ましい。このような増量剤を添加することにより、主 として検知感度を高めることができる。

【0022】本発明で使用できる溶剤としては、通常、印刷用、筆記用等のインキ組成物に用いられる溶剤であればいずれも使用できる。例えば、アルコール系、エステル系、エーテル系、ケトン系、炭化水素系等の各種溶剤が使用でき、使用する染料、樹脂系バインダーの溶解性等に応じて適宜選択すれば良い。

【0023】これらの配合割合は用いる成分の種類、用途等に応じて適宜設定すれば良い。例えば、オゾン検知用インキとして上記アントラキノン系染料を含有するインキを用いる場合は、通常はインキ中アントラキノン系染料0.05~5重量%(好ましくは0.1~1重量%)とし、樹脂系バインダー50重量%以下(好ましくは5~35重量%)、増量剤1~30重量%(好ましくは2~20重量%)等で調整すれば良い。

50 【0024】また、カチオン系界面活性剤をさらに配合

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する場合は、通常はインキ中アントラキノン系染料 0. 05~10重量%(好ましくは0.1~1重量%)、カ チオン系界面活性剤0.2~30重量%(好ましくは 0.5~10重量%)とした上で、樹脂系バインダー5 ○重量%以下(好ましくは5~35重量%)、増量剤1 ~30重量% (好ましくは2~20重量%) 等で調整す れば良い。

【0025】これら各成分は、同時に又は順次に配合 し、ホモジナイザー、デゾルバー等の公知の攪拌機を用 いて均一に混合すれば良い。例えば、まず溶剤にアント 10 ラキノン系染料、カチオン系界面活性剤、樹脂系バイン ダー、増量剤等を順に配合し、混合・攪拌すれば良い。 【0026】一方、オーバーコート層は、上記変色層上 の一部又は全部に形成される。本発明では、変色層がオ ゾン雰囲気にさらされる部分の全体にオーバーコート層 が形成されることが望ましい。オーバーコート層は、必 要に応じて2層以上を形成しても良い。

【0027】オーバーコート層は、造膜性高分子を含む ことが好ましい。特に実質的に造膜性高分子のみからな ることが好ましい。これにより、変色層の変色をより確 20 実かつ容易に認識することができる。従って、本発明で は、オーバーコート層は着色剤を含有しないことが望ま

【0028】本発明では、造膜性高分子として水溶性高 分子を好適に用いることができる。特にその種類は限定 されず、オゾンイジケーターの性能、使用目的等に応じ て公知の水溶性高分子の中から適宜選ぶことができる。 例えば、ポリビニルアルコール、ポリエチレングリコー ル、ポリプロピレングリコール、ポリアクリルアミド、 ッド、ポリビニルエーテル、ポリマレイン酸共重合体、 ポリエチレンイミン等の水溶性樹脂のほか、可溶性デン プン、カルボキシルデンプン、ブリティッシュゴム、ジ アルデヒドデンプン、デキストリン、カチオンデンプン 等のデンプン類; ビスコース、メチルセルロース、エチ ルセルロース、カルボキシメチルセルロース、ヒドロキ シエチルセルロース等のセルロース類等が挙げられる。 これらは1種又は2種以上で使用することができる。こ の中でも、特にカルボキシメチルセルロース、ヒドロキ シエチルセルロース、ポリビニルアルコール、ポリエチ 40 レングリコール、ポリプロピレングリコール等が好まし

【0029】また、水溶性高分子以外の造膜性高分子と しては、例えばマレイン酸樹脂、アミド樹脂、ケトン樹 脂、アルキルフェノール樹脂、ロジン変性樹脂、ポリビ ニルブチラール、ポリビニルピロリドン、セルロース系 樹脂、アクリル系樹脂、酢酸ビニル系樹脂等が挙げられ る。これらは、エマルジョン樹脂として使用することも できる。

【0030】オーバーコート層の形成は、例えば造膜性 50 【0037】本発明オゾンインジケーターでは、変色

高分子を水、アルコール類等の水性溶媒(特に水が好ま しい。) に溶解させたコート溶液を用いて行うことがで きる。この場合、オーバーコート層は実質的に水溶性高 分子のみからなる。

【0031】コート溶液中の造膜性高分子の濃度は、造 膜性高分子の種類、所望のオゾンインジケーター感度等 に応じて適宜設定すれば良いが、通常は1~30重量% 程度、好ましくは5~25重量%とすれば良い。

【0032】コート溶液には、本発明の効果を妨げない 範囲内で消泡剤等の添加剤を配合することもできる。

【0033】本発明では、変色層及びオーバーコート層 のほかに、必要に応じてオゾンの存在下でも変色しない 層である非変色層を設けることもできる。非変色層の形 成により、変色がより容易に識別でき、かつ、デザイン も自由にできる。

【0034】非変色層は、通常はオゾンにより変色しな いインキによって形成することができる。また、非変色 層は、オゾンにより変色しない限りは基材そのものも包 含する。従って、例えばオゾンにより変色しない基材上 にオゾン検知用インキによって変色層が形成されたもの も本発明オゾンインジケーターとして用いることができ る。また、例えばオゾンにより変色しない基材(紙、不 織布等)にオゾン検知用インキを含浸させることにより 変色層が形成されたものも本発明オゾンインジケーター として用いることができる。この場合は、上記基材が非 変色層となる。非変色層の形成も、変色層と同様にして 行うことができる。

【0035】非変色層を形成するためのインキとして は、オゾンにより変色しない限りいずれのインキも用い ポリアクリル酸、ポリビニルピロリドン、水溶性アルキ 30 ることができる。このようなインキとして、市販の普通 色インキも使用できる。例えば、水性インキ、油性イン キ、無溶剤型インキ等を用いることができる。また、印 刷する場合は印刷方法に応じて公知の凸版インキ、グラ ビアインキ、スクリーンインキ、オフセットインキ等を 適宜使い分けることができる。これらのインキは、その まま単独で用いたり、あるいは2種以上を混合して調色 しても良い。また、非変色層におけるインキには、公知 のインキに配合されている成分(例えば、樹脂系バイン ダー、増量剤、溶剤等)が含まれていても良い。

> 【0036】本発明における変色層、非変色層及びオー バーコート層の形成は、シルクスクリーン印刷、グラビ ア印刷、オフセット印刷、凸版印刷、フレキソ印刷等の 公知の印刷方法に従って行うことができる。また、基材 をオゾン検知用インキ中に浸漬することによって各層を 形成することもできる。紙、不織布等のようにインキが 浸透する材料には特に好適である。なお、変色層、非変 色及びオーバーコート層の厚さは、各層で使用する原料 の種類、オゾンインジケーターの使用目的等に応じて適 宜設定すれば良い。

層、非変色層及びオーバーコート層はそれぞれ1層ずつ 形成しても良く、あるいはそれぞれ複数層を積層しても 良い。また、変色層どうしを積層しても良い。この場 合、変色層どうしが互いに同じ組成であっても又は異な る組成であっても良い。非変色層どうしを積層しても良 い。非変色層どうしが互いに同じ組成であっても又は異 なる組成であっても良い。同様に、オーバーコート層ど うしを積層する場合も、各層が互いに同じ組成であって も又は異なる組成であっても良い。

【0038】各層は、基材又は各層の全面に形成しても 10 良く、あるいは部分的に形成しても良い。この場合も、 変色層の変色が確保できるようなかたちで各層を形成す ることが必要である。

【 ○ ○ 3 9 】 非変色を形成する場合、特に基材上に①オゾン検知用インキからなる変色層、②非変色層、③当該変色層上の一部又は全部に形成されたオーバーコート層を有し、かつ、当該変色層の一部又は全部がオゾンにより変色できるように各層が形成されているオゾンインジケーターが好ましい。

【0040】変色層が変色できるようにするためには、例えば変色層の少なくとも一部がオゾン雰囲気に露出するように変色層上に非変色層を形成し、その露出している変色層の一部又は全部をオーバーコート層で被覆すれば良い。この場合、非変色層もオーバーコート層で被覆されていても良い。

【0041】また、変色層の変色によりはじめて変色層と非変色層との色差が識別できるように変色層及び非変色層を形成したり、あるいは変色によってはじめて変色層と非変色層との色差が生じないように形成することもできる。特に、変色してはじめて変色層と非変色層との 30色差が識別できるように変色層及び非変色層を形成することが好ましい。

【0042】色差が識別できるようにする場合には、例えば変色層の変色によりはじめて文字、図柄及び記号の少なくとも1つが出現するように変色層及び非変色層を形成することができる。本発明では、文字、図柄及び記号は、変色(すなわちオゾンの存在)を知らせるすべての情報を包含する。これら文字等は、使用目的等に応じて適宜デザインすれば良い。

【0043】また、変色前における変色層と非変色層と を互いに異なる色としても良いが、特に両者を実質的に 同じ色とし、変色後にはじめて変色層と非変色層との色 差(コントラスト)が識別できるようにしても良い。

【0044】本発明オゾンインジケーターでは、変色層と非変色層とが重ならないように変色層及び非変色層を形成しても良い。これにより、使用するインキ量を節約することもできる。例えば、基材の一部に変色層を形成し、残りの部分には非変色層を形成したり、あるいは基材のまま露出させても良い。

【0045】さらに、本発明では、変色層及び非変色層 50 を肉眼でも容易に検知できる。

の少なくとも一方の層上にさらに変色層又は非変色層を 形成しても良い。例えば、変色層と非変色層とが重なら ないように変色層及び非変色層を形成した層(「変色ー 非変色層」という)の上からさらに別のデザインを有す る変色層を形成すれば、変色ー非変色層における変色層 及び非変色層の境界線が実質的に識別できない状態にで きるので、より優れた外観を達成することができる。

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【0046】本発明のオゾンインジケーターは、これをオゾン雰囲気中に設置することによって、より正確かつ迅速にオゾン濃度及びCT値(オゾン濃度×暴露時間)を検知することができる。特に、本発明オゾンインジケーターはオーバーコート層を有することから、高濃度のオゾン雰囲気下でも定性的な検知はもとより、定量的な検知を実施することも可能である。例えば、オゾン濃度1000ppm以上、特に3000pm以上のオゾン雰囲気にも適用することができる。かかる点より、本発明のインジケーターは、食品、医療器具等の殺菌・消毒、手術室、無菌室等の特定雰囲気中における殺菌、消毒、消臭等に好適に用いることができる。

【0047】本発明では、特にCT値と色差(ΔE)との関係、CT値と変色域との関係等の既知のデータに基づいて、検出された色差、変色域の大きさ等からオゾン濃度、CT値等を定性的又は定量的に検知することもできる。例えば、本発明オゾンインジケーターの変色層に沿ってCT値に応じた目盛りを設けることにより、変色層の変色域の大きさに基づいて定量的にCT値を測定することもできる。さらに、得られたCT値に基づいて、オゾン濃度あるいは暴露時間を定量的又は定性的に測定することも可能である。

びますることが可能である。

[0049]

【発明の効果】本発明のオゾンインジケーターは、特定のオーバーコート層を有しているので、高濃度オゾン雰囲気下でも定性的・定量的にオゾンを検知することができる。特に、オゾン濃度1000ppm以上という高濃度でも定量的にオゾン濃度を測定することが可能である。

【0050】変色層として第一アミノ基及び第二アミノ 基の少なくとも1種のアミノ基を有するアントラキノン 系染料を用いる場合は、実質的に乾燥した状態であって もオゾンと効果的に反応して変色し、より優れた検知精 度(選択性)、感度、安定性等を発揮し、オゾンの存在 を内限でも変見に検知できる 9

【0051】また、上記アントラキノン系染料等の成分 の種類及び配合割合を変えることによって検知感度、変 色速度等を自由に制御でき、より確実にオゾン濃度を検 知することも可能である。さらに、オーバーコート層の 形成により、温度又は湿度に応じて変色度合が異なるよ うに設計することが可能である。

[0052]

【実施例】以下に実施例及び比較例を示し、本発明の特 徴をより詳細に説明する。但し、本発明は、これら実施 例に限定されるものではない。

【0053】実施例1

アントラキノン系分散染料(「ミケトンファストレッド バイオレットR」三井BASF社製)0. 4重量部、樹 脂系バインダーとしてエチルセルロース系樹脂(「エト セル10」ダウケミカル社製)7.5重量部、カチオン 系界面活性剤として塩化ヤシアルキルトリメチルアンモ ニウム (「CA-2150」NIKKOL社製) 2重量 部及び溶剤としてエチルセロソルブ(「シーホゾールM G | 日本触媒社製) 90.1重量部を均一に攪拌機によ り混合し、オゾン検知用インキを調製した。一方、オー 20 バーコート層の形成に用いるコート溶液として、カルボ キシメチルセルロース(「セロゲン5A」第一工業製薬 製)を水に溶解させた10重量%カルボキシメチルセル ロース水溶液を調製した。

【0054】基材(ケント紙)上に、上記オゾン検知用 インキを120メッシュのシルクスクリーンを用いてシ ルクスクリーン印刷することにより、基材全体に変色層 を形成した。次いで、この変色層の全体に上記コート溶 液を100メッシュのシルクスクリーンを用いてシルク ケーターを作製した。

【0055】実施例2

アントラキノン系分散染料(「ミケトンファストレッド バイオレットR | 三井BASF社製)〇. 9重量部、樹 脂系バインダーとしてエチルセルロース系樹脂(「エト セル10」ダウケミカル社製)7.5重量部、カチオン 系界面活性剤として塩化ヤシアルキルトリメチルアンモ ニウム(「CA-2150」NIKKOL社製)2重量 部、シリカゲル(「アエロジルR-972」日本アエロ ジル社製)10重量部及び溶剤としてエチルセロソルブ 40 (「シーホゾールMG」日本触媒社製)89.6重量部 を均一に攪拌機により混合し、オゾン検知用インキを調 製した。

【0056】基材(ケント紙)上に、上記オゾン検知用

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インキを120メッシュのシルクスクリーンを用いてシ ルクスクリーン印刷することにより、基材全体に変色層 を形成した。次いで、この変色層の全体に実施例1と同 じコート溶液を実施例1と同様にしてシルクスクリーン 印刷することにより、シート状オゾンインジケーターを 作製した。

【0057】比較例1

オーバーコート層を形成しないほかは、実施例1と同様 にしてシート状オゾンインジケーターを作製した。

10 【0058】比較例2

オーバーコート層を形成しないほかは、実施例2と同様 にしてシート状オゾンインジケーターを作製した。

【0059】試験例1

各実施例及び比較例で作製された各オゾンインジケータ ーについて、CT値依存性、温度依存性及び湿度依存性 を調べた。これらの結果を図1に示す。

【0060】CT値依存性は、温度25℃、相対温度9 5%RHの条件下において、CT値を70000から7 56000の範囲で変化させた場合の変色性を色差△E で評価した。

【0061】湿度依存性は、温度25℃、CT値470 000の条件下において、相対湿度を30%RH、70 %RH及び95%RHと変化させた場合の変色性を色差 ΔE で評価した。

【0062】温度依存性は、CT値400000、相対 湿度95%RHの条件下において、温度を10℃、25 ℃及び40℃と変化させた場合の変色性を色差△Eで評 価した。

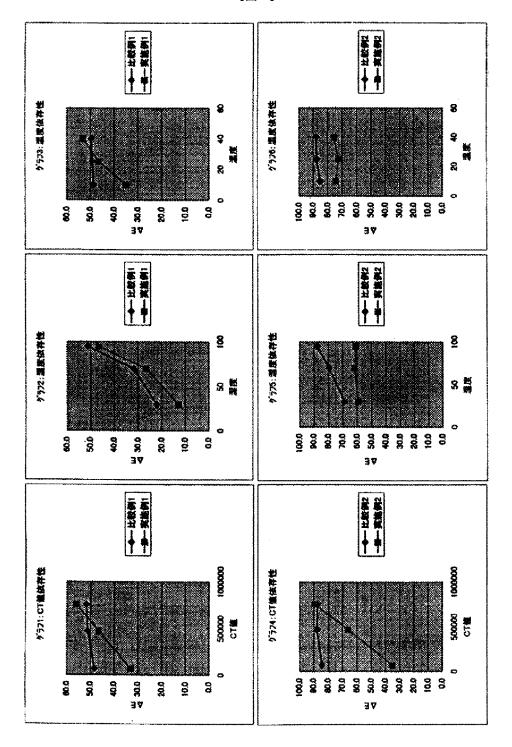
【0063】図1の結果からも明らかなように、本発明 スクリーン印刷することにより、シート状オゾンインジ 30 オゾンインジケーターは、CT値の違いによって明確な 変色が認められ、比較的高い濃度でもオゾンを確実に検 知できることがわかる。

> 【0064】さらに、実施例1では湿度又は温度によっ ても変色度合が異なるのに対し、実施例2では湿度又は 温度による変色度合に変化がないことがかわる。すなわ ち、本発明オゾンインジケーターによれば、CT値依存 性のほか、湿度依存性及び温度依存性を自由に制御でき ることもわかる。

【図面の簡単な説明】

【図1】試験例1の結果を示す図である。グラフ1及び 4はCT値依存性について調べた結果、グラフ2及び5 は湿度依存性について調べた結果、グラフ3及び6は温 度依存性について調べた結果を示す。

【図1】



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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to an ozone indicator and an ozone level measuring method.

[0002]

[Description of the Prior Art]Since ozone is excellent in the disinfection, it is used for sterilization and disinfection of foodstuffs and instruments, the sterilization and disinfection in fixed atmosphere like the operating room of a hospital, or deodorization. On the other hand, toxicity of ozone is very strong, and since a human body is also affected, the threshold limit value has a limit. On the other hand, in a photochemical smog forecast, the level of oxidants in the atmosphere serves as an important element.

[0003]For this reason, that detection method is developed variously that an ozone level should be supervised. As an ozone (oxidant) detection method in the former, discoloration by the reaction of a lower type (1) is mainly used.

(O)
$$K I \rightarrow I_2 \qquad \cdots (1)$$

The method of measuring optically the discoloration degree which introduced the gas which contains ozone in an iodination potash solution, for example as a detection method using this principle, and is proportional to the quantity of the iodine by which it is generated with a color comparator, or the method by an indicator tube simple type is known conventionally. [0004]

[Problem(s) to be Solved by the Invention]However, these detection methods are not suitable for high-concentration ozone detection for the purpose of detection of ozone of comparatively low concentration [all]. That is, even if it is going to detect high-concentration ozone by these methods and the existence of ozone is detectable since it discolors in an instant, an ozone level, a CT valve (an ozone level and the integrated value of time of exposure), etc. are quantitatively undetectable.

[0005]Therefore, the main purposes of this invention are to provide especially the ozone indicator

http://www4.ipdl.inpit.go.jp/cgi-bin/tran_web_cgi_ejje?atw_u=http%3A%2F%2Fwww4.ipdl... 11/26/2008

which can measure an ozone level etc. also under high-concentration-ozone atmosphere. [0006]

[Means for Solving the Problem]As a result of repeating research wholeheartedly in view of a problem of this conventional technology, this invention person finds out that the above-mentioned purpose can be attained with an ozone indicator with specific composition, and came to complete this invention.

[0007]namely, a changing layer which this invention becomes from ink for ** ozone detection at least and ** -- an ozone indicator having a part or an overcoat layer which boiled all and was formed on the changing layer concerned is started.

[0008]This invention relates to a measuring method of an ozone level calculating a CT valve by color difference or a transition interval by discoloration of a changing layer, after installing the above-mentioned ozone indicator into ozone atmosphere.

[0009]

[Embodiment of the Invention]the changing layer which the ozone indicator of this invention becomes from the ink for ** ozone detection at least, and ** -- it has the part or the overcoat layer which boiled all and was formed on the changing layer concerned

[0010]The above-mentioned changing layer is a layer discolored under existence of ozone, and is formed mainly in the ink for ozone detection. "Discoloration" in this invention is a concept which includes all the phenomena which change the original colors (brightness, hue, etc.), for example, tenebrescence, decolorization, coloring, etc. are included. A changing layer may be formed on a substrate, and if the changing layer itself has a moldability (shape retaining performance), even if he has no substrate, it can be formed.

[0011]When using a substrate, the kind in particular of the substrate is not restricted, for example, can use metal and an alloy, a woody material, paper, ceramics, glass, concrete, plastics, textiles (a nonwoven fabric, textile fabrics, other fibrous sheets), these composite materials, etc. [0012]The ink for ozone detection for forming a changing layer will not be restricted especially if it discolors by being exposed to ozone atmosphere (atmosphere containing ozone), but publicly known ink or commercial item can be used for it. For example, the ink using potassium iodide, a triphenylmethane series leuco, p-n-butoxyaniline, etc. can be used.

[0013]It is desirable to use the ink containing the anthraquinone dye which has at least one sort of amino groups of the first amino group and the second amino group as ink for ozone detection especially in this invention.

[0014]The anthraquinone dye used by this invention makes anthraquinone a basic skeleton, especially as long as it has at least one sort of amino groups of the first amino group and the second amino group, it is not restricted, but a publicly known anthraquinone system disperse dye etc. can be used for it. It may have the above-mentioned amino group two or more, and these may be mutually of the same kind, or may be different from each other.

[0015]As such anthraquinone dye, for example 1,4-diaminoanthraquinone (C. I.Disperse Violet 1), 1-amino-4-hydroxy-2-methoxy anthraquinone (C. I.Disperse Red 4), 1-amino-4-methylamino anthraquinone (C. I.Disperse Violet 4), 1,4-diamino-2-methoxy anthraquinone (C. I.DisperseRed 11), 1-amino-2-methylanthraquinone (C. I.Disperse Orange 11), 1-amino-4-hydroxyanthraquinone

(C. I.Disperse Red 15), 1,4,5,8-tetraminoanthraquinone (C. I.Disperse Blue 1), 1,4-diamino-5-nitroanthraquinone (C. I.DisperseViolet 8), etc. can be mentioned (the inside of a parenthesis is a color number). In addition, C.I.Solvent Blue. 14 and C.I.Solvent Blue. 63 and C.I.Solvent Violet. 13 and C.I.SolventViolet. 14, C.I.Solvent Red 52, C.I.Solvent Red 114, C.I.Vat Blue 21, C.I.VatBlue 30, C.I.Vat Violet 15, and C.I.Vat Violet. 17, C.I.Vat Red 19, and C.I.Vat. Red 28 and C.I.Acid Blue. 23, C.I.Acid Blue 80, and C.I.Acid. Violet 43 and C.I.Acid Violet. The color known as 48, C.I.Acid Red 81, C.I.Acid Red 83, C.I.Reactive Blue 4, C.I.Reactive Blue 19, and C.I.Disperse Blue 7 grade can also be used. These anthraquinone dye is independent or can be used together two or more sorts. Also in these anthraquinone dye, C.I Disperse Blue7 and C.I Disperse Violet 1 grade are preferred. The detecting sensitivity of ozone is also controllable by this invention by changing the kinds (molecular structure etc.) of these anthraquinone dye. [0016]It is more preferred to contain further a quarternary-ammonium-salt type cation system

[0016]It is more preferred to contain further a quarternary-ammonium-salt type cation system surface-active agent in the ink containing the above-mentioned anthraquinone dye in this invention.

[0017]Especially as an above-mentioned quarternary-ammonium-salt type cation system surface-active agent (only henceforth a "cation system surface-active agent"), it cannot be restricted, but alkyl ammonium salt can usually be used, and this can also use a commercial item. These can be used by one sort or two sorts or more. In this invention, the more outstanding ozone detecting sensitivity can be obtained by using together these cation system surface-active agent with said anthraquinone dye.

[0018]Also in these cation system surface-active agent, alkyl trimethylammonium salt, a dialkyl dimethylannmonium salt, etc. are preferred. Specifically Chloridation coconut alkyl trimethylammonium, chloridation beef tallow alkyl trimethylammonium, Chloridation behenyl trimethylammonium, hexadecyl chloride trimethylammonium, Chloridation lauryl trimethylammonium, octadecyl chloride trimethylammonium, Dioctyl chloride dimethylannmonium, chloridation distearyldimethylbenzylammonium, alkyl chloride benzyl dimethylannmonium, etc. are mentioned, and especially chloridation lauryl trimethylammonium is preferred.

[0019]In the ink of this invention, the ingredient used for publicly known ink, such as a resin system binder, an extender, and a solvent, if needed can be blended suitably.

[0020]The publicly known resinous principle which should just choose suitably as a resin system binder according to the kind of substrate, etc., for example, is used for the ink compositions the object for a note, for printing, etc. is employable as it is. Specifically, maleic acid resin, amide resin, ketone resin, alkylphenol resin, rosin modified resin, a polyvinyl butyral, a polyvinyl pyrrolidone, cellulose type resin, acrylic resin, vinyl acetate system resin, etc. can be mentioned, for example.

[0021]Especially as an extender, it is not restricted, for example, bentonite, activated clay, an aluminum oxide, silica gel, etc. can be mentioned. In addition, the material known can be used as a publicly known extender. Also in this, a porous thing is preferred and especially silica gel is more preferred. By adding such an extender, detecting sensitivity can mainly be raised.

[0022]As a solvent which can be used by this invention, if it is a solvent used for the ink compositions the object for printing, for a note, etc., all can usually be used. For example, various

solvents, such as an alcohol system, an ester system, an ether system, a ketone system, and a hydrocarbon system, can be used, and what is necessary is just to choose suitably according to the solubility etc. of the color to be used and a resin system binder.

[0023]What is necessary is just to set up these blending ratios suitably according to the kind of ingredient to be used, a use, etc. For example, when using the ink containing the above-mentioned anthraquinone dye as ink for ozone detection, Usually, what is necessary is to consider it as 0.05 to 5 % of the weight (preferably 0.1 to 1 % of the weight) of anthraquinone dye in ink, and for 50 or less (preferably 5 to 35 % of the weight) % of the weight of resin system binders, 1 to 30 % of the weight (preferably 2 to 20 % of the weight) of extenders, etc. just to adjust. [0024]When blending a cation system surface-active agent further, Usually, after considering it as 0.05 to 10 % of the weight (preferably 0.1 to 1 % of the weight) of anthraquinone dye in ink, and 0.2 to 30 % of the weight (preferably 0.5 to 10 % of the weight) of cation system surface-active agents, What is necessary is for 50 or less (preferably 5 to 35 % of the weight) % of the weight of resin system binders, 1 to 30 % of the weight (preferably 2 to 20 % of the weight) of extenders, etc. just to adjust.

[0025]What is necessary is to blend these each ingredient being simultaneous or one by one, and just to mix it uniformly using publicly known agitators, such as a homogenizer and a desolver. For example, what is necessary is to blend anthraquinone dye, a cation system surface-active agent, a resin system binder, an extender, etc. with a solvent in order first, and just to mix and stir. [0026]On the other hand, an overcoat layer is formed in some or all on the above-mentioned changing layer. It is desirable to form an overcoat layer in the whole portion in which a changing layer is exposed to ozone atmosphere in this invention. An overcoat layer may form more than two-layer if needed.

[0027]As for an overcoat layer, it is preferred that film formability polymers are included. It is preferred to consist only of film formability polymers substantially especially. Thereby, discoloration of a changing layer can be recognized more certainly and easily. Therefore, as for an overcoat layer, in this invention, it is desirable not to contain colorant.

[0028]In this invention, a water soluble polymer can be conveniently used as film formability polymers. The kind in particular is not limited but can be suitably chosen from publicly known water soluble polymers according to the performance of OZONI Decatur, the purpose of use, etc. For example, polyvinyl alcohol, a polyethylene glycol, a polypropylene glycol, Polyacrylamide, polyacrylic acid, a polyvinyl pyrrolidone, water-soluble alkyd, Water soluble resin, such as polyvinyl ether, a polymer lane acid copolymer, and polyethyleneimine, etc. Soluble starch, carboxyl starch, British rubber, dialdehyde starch, Starch, such as dextrin and cation starch; cellulose, such as viscose, methyl cellulose, ethyl cellulose, carboxymethyl cellulose, and hydroxyethyl cellulose, is mentioned. These can be used by one sort or two sorts or more. Also in this, carboxymethyl cellulose, hydroxyethyl cellulose, polyvinyl alcohol, a polyethylene glycol, a polypropylene glycol, etc. are especially preferred.

[0029]As film formability polymers other than a water soluble polymer, maleic acid resin, amide resin, ketone resin, alkylphenol resin, rosin modified resin, a polyvinyl butyral, a polyvinyl pyrrolidone, cellulose type resin, acrylic resin, vinyl acetate system resin, etc. are mentioned, for

example. These can also be used as emulsion resin.

[0030]Formation of an overcoat layer can be performed using the coat solution in which aqueous solvents (especially water is preferred.), such as water and alcohols, were made to dissolve film formability polymers for example. In this case, an overcoat layer consists only of water soluble polymers substantially.

[0031]What is necessary is just to usually make it into 5 to 25 % of the weight preferably about 1 to 30% of the weight, although what is necessary is just to set up suitably the concentration of the film formability polymers in a coat solution according to the kind of film formability polymers, desired ozone indicator sensitivity, etc.

[0032]Additive agents, such as a defoaming agent, can also be blended with a coat solution within limits which do not bar the effect of this invention.

[0033]In this invention, the non-changing layer which is a layer which is not discolored under existence of ozone if needed can also be provided besides a changing layer and an overcoat layer. By formation of a non-changing layer, discoloration can identify more easily and a design can also be freed.

[0034]A non-changing layer can be formed in the ink which is not usually discolored by ozone. A non-changing layer includes the substrate itself, unless it discolors by ozone. Therefore, that by which the changing layer was formed in the ink for ozone detection on the substrate which is not discolored, for example by ozone can also be used as this invention ozone indicator. That in which the changing layer was formed can also be used as this invention ozone indicator by impregnating with the ink for ozone detection the substrates (paper, a nonwoven fabric, etc.) which are not discolored, for example by ozone. In this case, the above-mentioned substrate serves as a non-changing layer. Formation of a non-changing layer as well as a changing layer can be performed. [0035]As ink for forming a non-changing layer, unless it discolors by ozone, any ink can be used. Commercial common color ink can also be used as such ink. For example, water color ink, oil based ink, solventless type ink, etc. can be used. When printing, according to a printing method, publicly known letterpress ink, gravure ink, screen ink, offset ink, etc. can be used properly suitably. These ink may be used independently as they are, or may mix and tone two or more sorts. The ingredients (for example, a resin system binder, an extender, a solvent, etc.) blended with publicly known ink may be contained in the ink in a non-changing layer.

[0036]Formation of the changing layer in this invention, a non-changing layer, and an overcoat layer can be performed in accordance with publicly known printing methods, such as silk screen printing, gravure printing, offset printing, Toppan Printing, and flexographic printing. Each class can also be formed by immersing a substrate into the ink for ozone detection. It is suitable for paper and especially the material that ink permeates like a nonwoven fabric. What is necessary is just to set up suitably the thickness of a changing layer, un-discoloring, and an overcoat layer according to the kind of raw material used on each class, the purpose of using an ozone indicator, etc.

[0037]In this invention ozone indicator, it may form a changing layer, a non-changing layer, and one layer of overcoat layers at a time, respectively, or they may laminate two or more layers, respectively. Changing layers may be laminated. In this case, it may be a presentation which is

different even if changing layers are the same presentations mutually. Non-changing layers may be laminated. It may be a presentation which is different even if non-changing layers are the same presentations mutually. Similarly, when laminating overcoat layers, it may be a presentation which is different even if each class is the same presentation mutually.

[0038]Each class may be formed all over a substrate or each class, or may be formed selectively. It is required to form each class in the form [like] which discoloration of a changing layer can secure also in this case.

[0039]The changing layer which consists of ink for ** ozone detection especially on a substrate when forming un-discoloring, ** a non-changing layer and ** -- the ozone indicator with which each class is formed so that it may have the part or the overcoat layer which boiled all and was formed on the changing layer concerned and a part or all of the changing layer concerned can discolor by ozone is preferred.

[0040]What is necessary is to form a non-changing layer on a changing layer so that at least a part of changing layer may be exposed to ozone atmosphere, for example, and just to cover the a part or all of a changing layer that has been exposed with an overcoat layer, in order to be able to discolor a changing layer. In this case, the non-changing layer may also be covered with the overcoat layer.

[0041]A changing layer and a non-changing layer can be formed so that the color difference of a changing layer and a non-changing layer cannot be identified without discoloration of a changing layer, or it can also form so that the color difference of a changing layer and a non-changing layer may not arise for the first time by discoloration. It is preferred to form a changing layer and a non-changing layer so that the color difference of a changing layer and a non-changing layer can be especially identified only after discoloring.

[0042]When enabling it to identify color difference, a changing layer and a non-changing layer can be formed so that at least one of a character, a pattern, and the signs may not appear without discoloration of a changing layer, for example. In this invention, a character, a pattern, and a sign include all the information which tells discoloration (namely, existence of ozone). What is necessary is just to design these characters suitably according to the purpose of use etc. [0043]Although it is good also as a color which is mutually different in the changing layer and the non-changing layer before discoloration, especially both are substantially made into the same color, and it may enable it to identify the color difference (contrast) of a changing layer and a non-changing layer for the first time after discoloration.

[0044]In this invention ozone indicator, a changing layer and a non-changing layer may be formed so that a changing layer and a non-changing layer may not lap. Thereby, the ink amount to be used can also be saved. For example, a changing layer may be formed in some substrates, and a non-changing layer may be formed in the remaining portion, or it may be made to expose with a substrate.

[0045]In this invention, a changing layer or a non-changing layer may be further formed on at least one layer of a changing layer and a non-changing layer. For example, if the changing layer which has another design from the layer (it is called "a discoloration-non-changing layer") in which the changing layer and the non-changing layer were formed is formed so that a changing layer and a

non-changing layer may not lap, Since the boundary line of the changing layer in a discoloration-non-changing layer and a non-changing layer changes into the state of not being substantially discriminable, the more outstanding appearance can be attained.

[0046]The ozone indicator of this invention can detect an ozone level and a CT valve (ozone level x time of exposure) more correctly and promptly by installing this into ozone atmosphere. It is also possible for detection qualitative also under a high-concentration ozone atmosphere to carry out quantitive detection from the first from especially this invention ozone indicator having an overcoat layer. For example, it is [ozone level of not less than 1000 ppm] especially applicable also to the ozone atmosphere of 3000 or more pm. From this point, the indicator of this invention can be used conveniently for the sterilization in the specific atmosphere of sterilization and disinfection of foodstuffs, a medical device, etc., an operating room, a germfree room, etc., disinfection, deodorization, etc.

[0047]In especially this invention, an ozone level, a CT valve, etc. are also qualitatively or quantitatively detectable from the size etc. of the detected color difference and a transition interval based on the known data of the relation between a CT valve and color difference (deltaE), the relation between a CT valve and a transition interval, etc. For example, based on the size of the transition interval of a changing layer, a CT valve can also be quantitatively measured by forming the graduation according to a CT valve along with the changing layer of this invention ozone indicator. It is also possible to measure an ozone level or time of exposure quantitatively or qualitatively based on the obtained CT valve.

[0048]Temperature dependence, humidity dependency, etc. besides a CT valve dependency are controllable to an ozone indicator. For example, at a specific temperature or humidity, it can control so that a discoloration degree becomes high, or it can control so that a discoloration degree becomes low (it stops or discoloring like). That is, it is possible to design in this invention ozone indicator, so that discoloration degrees may differ according to the conditions of humidity or temperature.

[0049]

[Effect of the Invention]Since the ozone indicator of this invention has a specific overcoat layer, it can detect ozone qualitatively and quantitatively also under high-concentration-ozone atmosphere. It is possible for high concentration called the ozone level of not less than 1000 ppm to also measure an ozone level quantitatively especially.

[0050]When using the anthraquinone dye which has at least one sort of amino groups of the first amino group and the second amino group as a changing layer, Even if it is in the substantially dry state, it reacts to ozone effectively, and it discolors, more outstanding detection precision (selectivity), sensitivity, stability, etc. are demonstrated, and, also with the naked eye, existence of ozone can be detected easily.

[0051]It is also possible by changing the kind and blending ratios of an ingredient, such as the above-mentioned anthraquinone dye, to be able to control detecting sensitivity, discoloration speed, etc. freely and to detect an ozone level more certainly. It is possible to design by formation of an overcoat layer, so that discoloration degrees may differ according to temperature or humidity.

[0052]

[Example]An example and a comparative example are shown below and the feature of this invention is explained more to details. However, this invention is not limited to these examples. [0053]Example 1 anthraquinone system disperse dye (made by "MIKETON fast red violet R" Mitsui BASF A.G.) 0.4 weight section, As a resin system binder, ethyl cellulose system resin (made by the "ethocell 10" Dow Chemical Co.) 7.5 weight section, Ethylcellosolve (made by "SHIHOZORU MG" NIPPON SHOKUBAI Co., Ltd.) 90.1 weight section was uniformly mixed with the agitator as a cation system surface-active agent as the amount part of chloridation coconut alkyl trimethylammonium (made by "CA-2150" NIKKOL) duplexs, and a solvent, and the ink for ozone detection was prepared. On the other hand, the 10-% of the weight carboxymethyl cellulose solution made to dissolve carboxymethyl cellulose (made by "cello gene 5A" Dai-Ichi Kogyo Seiyaku) in water was prepared as a coat solution used for formation of an overcoat layer. [0054] The changing layer was formed in the whole substrate by using the silk screen of 120 meshes and carrying out silk screen printing of the above-mentioned ink for ozone detection on a substrate (Kent paper). Subsequently, the sheet-shaped ozone indicator was produced by using the silk screen of 100 meshes for this whole changing layer, and carrying out silk screen printing of the above-mentioned coat solution to it.

[0055]Example 2 anthraquinone system disperse dye (made by "MIKETON fast red violet R" Mitsui BASF A.G.) 0.9 weight section, As a resin system binder, ethyl cellulose system resin (made by the "ethocell 10" Dow Chemical Co.) 7.5 weight section, As a cation system surface-active agent, the amount part of chloridation coconut alkyl trimethylammonium (made by "CA-2150" NIKKOL) duplexs, Ethylcellosolve (made by "SHIHOZORU MG" NIPPON SHOKUBAI Co., Ltd.) 89.6 weight section was uniformly mixed with the agitator as silica gel (made by "Aerosil R-972" Japan Aerosil) 10 weight section, and a solvent, and the ink for ozone detection was prepared.

[0056]The changing layer was formed in the whole substrate by using the silk screen of 120 meshes and carrying out silk screen printing of the above-mentioned ink for ozone detection on a substrate (Kent paper). Subsequently, the sheet-shaped ozone indicator was produced by carrying out silk screen printing of the same coat solution as Example 1 to this whole changing layer like Example 1.

[0057]Comparative example 1 overcoat layer was not formed, and also the sheet-shaped ozone indicator was produced like Example 1.

[0058]Comparative example 2 overcoat layer was not formed, and also the sheet-shaped ozone indicator was produced like Example 2.

[0059]About each ozone indicator produced by example of examination 1 each example, and a comparative example, a CT valve dependency, temperature dependence, and humidity dependency were investigated. These results are shown in drawing 1.

[0060]The CT valve dependency evaluated the allochroism at the time of changing a CT valve from 70000 in 756000 under the temperature of 25 **, and the condition of 95% of relative humidity RH by color difference deltaE.

[0061] Humidity dependency evaluated the allochroism at the time of changing relative humidity

with RH, 70%RH, and 95%RH 30% under the temperature of 25 **, and the condition of CT valve 470000 by color difference deltaE.

[0062]Temperature dependence evaluated the allochroism at the time of changing temperature with 10 **, 25 **, and 40 ** under CT valve 400000 and the condition of 95% of relative humidity RH by color difference deltaE.

[0063]It turns out that clear discoloration is accepted by the difference in a CT valve, and this invention ozone indicator can detect ozone certainly also by comparatively high concentration by it so that clearly also from the result of drawing 1.

[0064]In Example 1, it changes to a discoloration degree changing also with humidity or temperature that there is no change in the discoloration degree by humidity or temperature by Example 2. That is, according to this invention ozone indicator, it also turns out that humidity dependency and temperature dependence besides a CT valve dependency are freely controllable.

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CLAIMS

[Claim(s)]

[Claim 1]a changing layer which consists of ink for ** ozone detection at least, and ** -- an ozone indicator having a part or an overcoat layer which boiled all and was formed on the changing layer concerned.

[Claim 2] The ozone indicator according to claim 1 with which ink for ozone detection contains anthraquinone dye which has at least one sort of amino groups of the first amino group and the second amino group.

[Claim 3]The ozone indicator according to claim 2 with which ink for ozone detection contains a cation system surface-active agent of further a quarternary-ammonium-salt type.

[Claim 4]The ozone indicator according to claim 3 whose quarternary-ammonium-salt type cation system surface-active agent is alkyl trimethylammonium salt.

[Claim 5] The ozone indicator according to any one of claims 2 to 4 with which ink for ozone detection contains an extender.

[Claim 6] The ozone indicator according to any one of claims 2 to 5 with which ink for ozone detection contains a resin system binder.

[Claim 7]The ozone indicator according to any one of claims 1 to 6 with which an overcoat layer contains film formability polymers.

[Claim 8] The ozone indicator according to claim 7 whose film formability resin is at least one sort of a water soluble polymer.

[Claim 9] The ozone indicator according to any one of claims 1 to 8 with which an overcoat layer does not contain colorant.

[Claim 10]A measuring method of an ozone level characterized by calculating a CT valve by color difference or a transition interval by discoloration of a changing layer after installing the ozone indicator according to any one of claims 1 to 9 into ozone atmosphere.

[Claim 11]The measuring method according to claim 10 whose ozone level in ozone atmosphere is not less than 1000 ppm.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]It is a figure showing the result of the example 1 of an examination. As a result of investigating the graphs 1 and 4 about a CT valve dependency and investigating the graphs 2 and 5 about humidity dependency, the graphs 3 and 6 show the result investigated about temperature dependence.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]However, these detection methods are not suitable for high-concentration ozone detection for the purpose of detection of ozone of comparatively low concentration [all]. That is, even if it is going to detect high-concentration ozone by these methods and the existence of ozone is detectable since it discolors in an instant, an ozone level, a CT valve (an ozone level and the integrated value of time of exposure), etc. are quantitatively undetectable.

[0005]Therefore, the main purposes of this invention are to provide especially the ozone indicator which can measure an ozone level etc. also under high-concentration-ozone atmosphere.

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MEANS

[Means for Solving the Problem]As a result of repeating research wholeheartedly in view of a problem of this conventional technology, this invention person finds out that the above-mentioned purpose can be attained with an ozone indicator with specific composition, and came to complete this invention.

[0007]namely, a changing layer which this invention becomes from ink for ** ozone detection at least and ** -- an ozone indicator having a part or an overcoat layer which boiled all and was formed on the changing layer concerned is started.

[0008] This invention relates to a measuring method of an ozone level calculating a CT valve by color difference or a transition interval by discoloration of a changing layer, after installing the above-mentioned ozone indicator into ozone atmosphere.

[0009]

[Embodiment of the Invention]the changing layer which the ozone indicator of this invention becomes from the ink for ** ozone detection at least, and ** -- it has the part or the overcoat layer which boiled all and was formed on the changing layer concerned

[0010]The above-mentioned changing layer is a layer discolored under existence of ozone, and is formed mainly in the ink for ozone detection. "Discoloration" in this invention is a concept which includes all the phenomena which change the original colors (brightness, hue, etc.), for example, tenebrescence, decolorization, coloring, etc. are included. A changing layer may be formed on a substrate, and if the changing layer itself has a moldability (shape retaining performance), even if he has no substrate, it can be formed.

[0011]When using a substrate, the kind in particular of the substrate is not restricted, for example, can use metal and an alloy, a woody material, paper, ceramics, glass, concrete, plastics, textiles (a nonwoven fabric, textile fabrics, other fibrous sheets), these composite materials, etc.

[0012] The ink for ozone detection for forming a changing layer will not be restricted especially if it discolors by being exposed to ozone atmosphere (atmosphere containing ozone), but publicly known ink or commercial item can be used for it. For example, the ink using potassium iodide, a triphenylmethane series leuco, p-n-butoxyaniline, etc. can be used.

[0013]It is desirable to use the ink containing the anthraquinone dye which has at least one sort of amino groups of the first amino group and the second amino group as ink for ozone detection

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especially in this invention.

[0014] The anthraquinone dye used by this invention makes anthraquinone a basic skeleton, especially as long as it has at least one sort of amino groups of the first amino group and the second amino group, it is not restricted, but a publicly known anthraquinone system disperse dye etc. can be used for it. It may have the above-mentioned amino group two or more, and these may be mutually of the same kind, or may be different from each other.

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EXAMPLE

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EFFECT OF THE INVENTION

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[0050]When using the anthraquinone dye which has at least one sort of amino groups of the first amino group and the second amino group as a changing layer, Even if it is in the substantially dry state, it reacts to ozone effectively, and it discolors, more outstanding detection precision (selectivity), sensitivity, stability, etc. are demonstrated, and, also with the naked eye, existence of ozone can be detected easily.

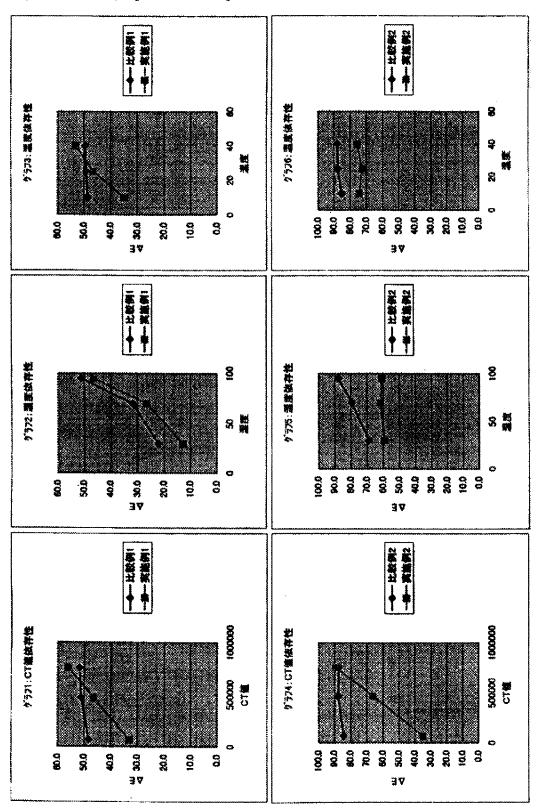
[0051]It is also possible by changing the kind and blending ratios of an ingredient, such as the above-mentioned anthraquinone dye, to be able to control detecting sensitivity, discoloration speed, etc. freely and to detect an ozone level more certainly. It is possible to design by formation of an overcoat layer, so that discoloration degrees may differ according to temperature or humidity.

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DRAWINGS

[Drawing 1]



[Translation done.]